

## Chlorotris(triphenylphosphine)silver\*

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**Abstract.**  $[\text{Ag}(\text{C}_{18}\text{H}_{15}\text{P})_3\text{Cl}]$ ,  $\text{C}_{54}\text{H}_{45}\text{AgClP}_3$ , monoclinic,  $P2_1/n$ ,  $a = 10.221$  (1),  $b = 33.735$  (4),  $c = 13.374$  (3) Å,  $\beta = 89.78$  (1)°,  $V = 4611$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.34$ ,  $D_o = 1.31$  Mg m<sup>-3</sup>. Final  $R = 0.054$ . The crystal structure is built up by the packing of discrete monomeric molecules. In these, Ag is tetrahedrally surrounded by three P atoms and one Cl atom. The coordination polyhedron is distorted, the angle range being 96.66 (5)–117.09 (4)°. A comparison is made

with the structure of chlorotris(triphenylphosphine)-copper(I).

**Introduction.** Single crystals of  $[\text{Ag}(\text{C}_{18}\text{H}_{15}\text{P})_3\text{Cl}]$ , in the following denoted  $[\text{Ag}(\text{Ph}_3\text{P})_3\text{Cl}]$ , were obtained from stoichiometric amounts of  $\text{AgNO}_3$ ,  $(\text{C}_2\text{H}_5)_4\text{NCl}$  and  $\text{Ph}_3\text{P}$  dissolved in warm  $\text{CH}_3\text{CN}$  after slow cooling of the solution. One crystal of approximate dimensions  $0.30 \times 0.25 \times 0.20$  mm along  $a$ ,  $b$  and  $c$  was selected for the intensity measurements. The crystal could be described by the ten planes (010), (010), (032), (03̄2), (03̄2), (03̄2), (13̄0), (13̄0), (110) and (110).

An Enraf–Nonius CAD-4 computer-controlled four-circle diffractometer equipped with a graphite mono-

\* Structures of Complexes Between Metal Halides and Phosphinothioethers or Related Ligands. IX.

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Table 1. Fractional coordinates (for Ag, Cl, P  $\times 10^5$ , for C  $\times 10^4$ ) and isotropic thermal parameters in  $[\text{Ag}(\text{Ph}_3\text{P})_3\text{Cl}]$

Standard deviations are given in parentheses.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å <sup>2</sup> )		<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å <sup>2</sup> )
Ag	20069 (4)	38906 (1)	27128 (3)	2.86 (2)	C(26)	1572 (6)	4567 (2)	5279 (4)	3.7 (1)
Cl	-2422 (13)	41903 (4)	30576 (12)	4.35 (4)	C(27)	1508 (6)	4927 (2)	5765 (5)	4.2 (1)
P(1)	17463 (13)	31945 (4)	19929 (10)	2.99 (3)	C(28)	2628 (6)	5099 (2)	6149 (4)	4.0 (1)
P(2)	28025 (12)	38956 (4)	45221 (9)	2.60 (3)	C(29)	3821 (6)	4910 (2)	6052 (5)	4.2 (1)
P(3)	30271 (13)	43858 (4)	15346 (10)	2.85 (3)	C(30)	3895 (6)	4542 (2)	5577 (4)	3.5 (1)
C(1)	85 (5)	3002 (2)	1926 (4)	3.1 (1)	C(31)	4468 (5)	3723 (1)	4736 (4)	2.9 (1)
C(2)	-249 (6)	2687 (2)	1311 (4)	4.1 (1)	C(32)	4845 (6)	3496 (2)	5550 (5)	4.2 (1)
C(3)	-1519 (7)	2544 (2)	1284 (5)	4.6 (1)	C(33)	6170 (8)	3402 (2)	5674 (5)	5.5 (1)
C(4)	-2473 (7)	2722 (2)	1862 (5)	5.5 (1)	C(34)	7091 (8)	3543 (2)	5015 (5)	5.5 (1)
C(5)	-2147 (8)	3031 (2)	2475 (6)	5.6 (2)	C(35)	6735 (7)	3765 (2)	4221 (5)	4.9 (1)
C(6)	-877 (6)	3174 (2)	2509 (5)	4.4 (1)	C(36)	5424 (6)	3851 (2)	4056 (4)	3.9 (1)
C(7)	2632 (5)	2807 (2)	2655 (4)	3.2 (1)	C(37)	2251 (5)	4437 (2)	311 (4)	3.2 (1)
C(8)	2094 (6)	2447 (2)	2930 (4)	4.1 (1)	C(38)	2944 (6)	4455 (2)	-585 (4)	4.1 (1)
C(9)	2821 (7)	2173 (2)	3499 (5)	5.3 (1)	C(39)	2250 (7)	4508 (2)	-1488 (5)	5.3 (1)
C(10)	4082 (8)	2270 (2)	3760 (5)	5.6 (1)	C(40)	930 (8)	4536 (2)	-1469 (6)	5.8 (2)
C(11)	4624 (7)	2621 (2)	3503 (5)	5.2 (1)	C(41)	228 (8)	4512 (2)	-598 (6)	5.7 (2)
C(12)	3912 (6)	2892 (2)	2954 (5)	4.3 (1)	C(42)	897 (6)	4463 (2)	307 (5)	4.3 (1)
C(13)	2287 (6)	3143 (2)	695 (4)	3.5 (1)	C(43)	4734 (5)	4264 (2)	1266 (4)	3.2 (1)
C(14)	3050 (9)	2846 (3)	342 (6)	6.6 (2)	C(44)	5778 (6)	4509 (2)	1484 (4)	4.0 (1)
C(15)	3404 (11)	2837 (3)	-692 (8)	9.0 (3)	C(45)	7058 (7)	4373 (2)	1368 (5)	5.1 (1)
C(16)	2982 (10)	3133 (3)	-1300 (7)	7.4 (2)	C(46)	7286 (8)	4002 (2)	1036 (6)	5.5 (1)
C(17)	2208 (8)	3419 (2)	-971 (6)	6.0 (2)	C(47)	6264 (8)	3755 (2)	783 (6)	5.9 (2)
C(18)	1837 (6)	3425 (2)	36 (5)	4.4 (1)	C(48)	4981 (7)	3887 (2)	907 (5)	5.0 (1)
C(19)	1760 (5)	3582 (1)	5304 (4)	2.9 (1)	C(49)	3032 (5)	4900 (2)	1961 (4)	3.1 (1)
C(20)	1377 (6)	3225 (2)	4915 (4)	3.9 (1)	C(50)	2551 (6)	4984 (2)	2909 (5)	4.4 (1)
C(21)	525 (7)	2977 (2)	5425 (5)	4.8 (1)	C(51)	2521 (8)	5373 (2)	3265 (5)	5.6 (2)
C(22)	20 (6)	3090 (2)	6334 (5)	4.3 (1)	C(52)	2953 (8)	5680 (2)	2658 (6)	5.8 (2)
C(23)	384 (7)	3441 (2)	6727 (5)	5.1 (1)	C(53)	3402 (7)	5599 (2)	1689 (5)	5.4 (1)
C(24)	1256 (7)	3692 (2)	6233 (5)	4.6 (1)	C(54)	3449 (6)	5211 (2)	1342 (5)	4.3 (1)
C(25)	2777 (5)	4369 (1)	5185 (3)	2.7 (1)					

Table 2. *Interatomic distances (Å) and angles (°) in [Ag(Ph<sub>3</sub>P)<sub>3</sub>Cl]*

Standard deviations are given in parentheses. For atom numbering see Fig. 1.

Ag—Cl	2.552 (1)	P(1)—Ag	2.552 (1)
—P(1)	2.552 (1)	—C(1)	1.822 (5)
—P(2)	2.556 (1)	—C(7)	1.823 (5)
—P(3)	2.520 (1)	—C(13)	1.827 (6)
P(2)—Ag	2.556 (1)	P(3)—Ag	2.520 (1)
—C(19)	1.826 (5)	—C(37)	1.829 (5)
—C(25)	1.826 (5)	—C(43)	1.826 (6)
—C(31)	1.823 (5)	—C(49)	1.825 (5)

Mean C—C distance in the phenyl rings 1.386 (3)\*

Cl—Ag—P(1)	109.72 (5)	Ag—P(1)—C(1)	116.5 (2)
Cl—Ag—P(2)	96.66 (5)	Ag—P(1)—C(7)	115.1 (2)
Cl—Ag—P(3)	102.75 (5)	Ag—P(1)—C(13)	114.5 (2)
P(1)—Ag—P(2)	113.41 (4)	C(1)—P(1)—C(7)	103.5 (2)
P(1)—Ag—P(3)	114.69 (5)	C(1)—P(1)—C(13)	101.4 (3)
P(2)—Ag—P(3)	117.09 (4)	C(7)—P(1)—C(13)	104.1 (3)
Ag—P(2)—C(19)	110.6 (2)	Ag—P(3)—C(37)	116.2 (2)
Ag—P(2)—C(25)	117.5 (2)	Ag—P(3)—C(43)	111.5 (2)
Ag—P(2)—C(31)	116.6 (2)	Ag—P(3)—C(49)	115.8 (2)
C(19)—P(2)—C(25)	102.7 (2)	C(37)—P(3)—C(43)	105.2 (2)
C(19)—P(2)—C(31)	105.6 (2)	C(37)—P(3)—C(49)	101.1 (2)
C(25)—P(2)—C(31)	102.4 (2)	C(43)—P(3)—C(49)	105.8 (2)

\* Cassel (1979).

chromator and Cu K $\alpha$  radiation was used in the data collection. The  $\omega$ - $2\theta$  scan technique, with a scan interval  $\Delta\omega = (0.60 + 0.25 \tan \theta)^\circ$ , was employed. The background was measured for one quarter of the scan time at each end of the peak-scan interval. In the range  $5 < \theta < 70^\circ$  7012 reflections with  $I > 2\sigma(I)$ , where  $\sigma(I)$  is the standard deviation based on counting statistics, were measured. The data set was scaled according to the intensities of two regularly measured standard reflections. The total intensity decrease was 10% and was linear with respect to exposure time. Corrections were also made for Lorentz, polarization, absorption [ $\mu(\text{Cu K}\alpha) = 5.4 \text{ mm}^{-1}$ ] (Busing & Levy, 1957), anomalous-dispersion and secondary-extinction (Zachariasen, 1967) effects.

Ag was located using the Patterson function. Successive electron density syntheses and least-squares refinements revealed the positions of Cl, P and C. Scattering factors for all atoms (neutral) were taken from *International Tables for X-ray Crystallography* (1974). The H atoms were geometrically positioned 1.00 Å from the corresponding C atoms, and with  $B = 5.0 \text{ Å}^2$  included in the final refinements. The quantity minimized was  $\sum w_i(|F_o| - |F_c|)^2$  giving final values of  $R = \sum |F_o| - |F_c| / \sum |F_o| = 0.054$  and  $R_w = [\sum w_i(|F_o| - |F_c|)^2 / \sum w_i |F_o|^2]^{1/2} = 0.063$ . Using  $w_i^{-1} = \sigma^2(F_o) + 0.010|F_o|^2 + 1.5$ , the average values of  $w_i(|F_o| - |F_c|)^2$  were made as constant as possible in different  $\sin \theta$  and  $|F_o|$  intervals. The value of  $S =$

Table 3. *Selected intramolecular distances (Å) between atoms of different ligands in [Ag(Ph<sub>3</sub>P)<sub>3</sub>Cl]*

The H atoms are positioned 1.00 Å from the corresponding C atoms in a regular trigonal-planar arrangement.

H...H distances	<3.00 Å	H(C42)...H(C18)	2.99
H(C50)...H(C26)	2.87	H(C50)...C(25)	2.86
H...C distances	<3.00 Å	H(C50)...C(26)	2.75
H(C20)...C(7)	2.58	H(C18)...C(37)	2.90
H(C20)...C(8)	2.95	H(C18)...C(42)	2.81
H(C20)...C(12)	2.95	H(C17)...C(39)	2.99
H(C48)...C(13)	2.76		
H(C48)...C(18)	2.80		
H...Cl distances	<3.40 Å	H(C42)...Cl	3.02
H(C6)...Cl	2.70	H(C50)...Cl	3.20
H(C26)...Cl	2.92		

$[\sum w_i(|F_o| - |F_c|)^2 / (m - n)]^{1/2}$  was 1.9. The secondary-extinction parameter  $g$  was  $0.69 \times 10^{-4}$ . In the final difference synthesis no peak larger than  $1.0 \text{ e Å}^{-3}$  was found.

Final positional and isotropic thermal parameters are given in Table 1,\* selected interatomic distances in Table 2 and some intramolecular H...H, H...C and H...Cl distances in Table 3. All calculations were made on the Univac 1108 computer in Lund.

**Discussion.** The crystal structure is built up by the packing of monomeric molecules of formula  $[\text{Ag}(\text{Ph}_3\text{P})_3\text{Cl}]$ . No H...H or H...Cl intermolecular distances shorter than 2.29 and 2.78 Å, respectively, are found. The van der Waals distances according to Pauling (1960) are 2.4 and 3.0 Å. According to Baur (1972) the radius of H is 1.00 Å, giving the van der Waals distances 2.0 and 2.8 Å for H...H and H...Cl, respectively. These intermolecular distances thus have normal values.

A stereoscopic view of the molecule is shown in Fig. 1. Ag is tetrahedrally surrounded by one Cl atom and three P atoms from three Ph<sub>3</sub>P ligands. As can be seen in Table 2 the tetrahedral angles around Ag deviate

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35454 (33 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

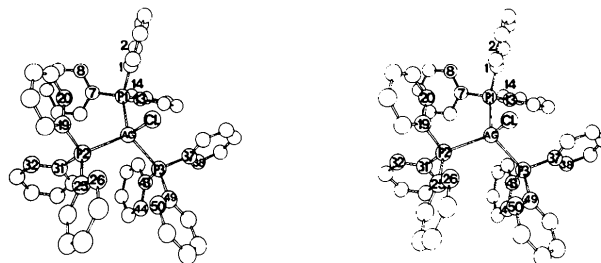


Fig. 1. A stereoscopic view of a molecule of  $[\text{Ag}(\text{Ph}_3\text{P})_3\text{Cl}]$ .

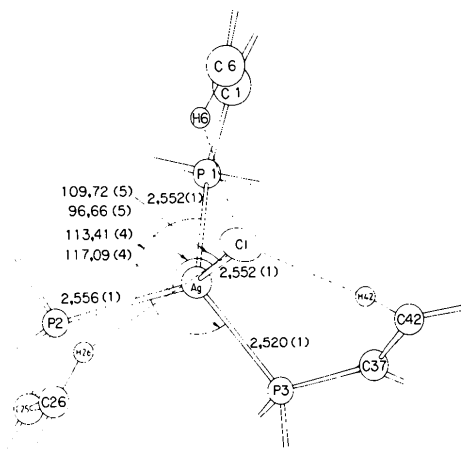


Fig. 2. A schematic drawing of a fragment of the  $[\text{Ag}(\text{Ph}_3\text{P})_3\text{Cl}]$  molecule. Selected distances (Å) and angles ( $^\circ$ ) are denoted. The intramolecular  $\text{H}\cdots\text{Cl}$  repulsive interactions are shown with broken lines.

significantly from the ideal value of  $109.5^\circ$ . All  $\text{P}-\text{Ag}-\text{Cl}$  angles are close to or smaller than  $109.5^\circ$ , all  $\text{P}-\text{Ag}-\text{P}$  greater than  $109.5^\circ$ . In Fig. 2 some distances and angles in the distorted tetrahedron around Ag are shown.

No silver halide phosphine structure of stoichiometry 1:1:3 has been reported in the literature. The structure of the analogous Cu compound,  $[\text{Cu}(\text{Ph}_3\text{P})_3\text{Cl}]$ , has been determined (Gill *et al.*, 1976). In this compound Cu is surrounded by three P atoms and one Cl, forming an almost ideal tetrahedron for all three independent molecules in the unit cell. The tetrahedral-angle range  $108.41(7)$ – $110.51(6)^\circ$  is found for the three molecules. There are indications that the differences between the two structures may be related to the difference between the tetrahedral covalent radii of Ag and Cu, *viz*  $0.17 \text{ \AA}$  (Pauling, 1960). The repulsive intramolecular  $\text{H}\cdots\text{H}$ ,  $\text{H}\cdots\text{C}$  and  $\text{H}\cdots\text{Cl}$  interactions between the ligands must be greater in the Cu compound; three equal, short intramolecular  $\text{H}\cdots\text{Cl}$  distances in each independent  $[\text{Cu}(\text{Ph}_3\text{P})_3\text{Cl}]$  molecule,  $2.66$ ,  $2.74$  and  $2.74 \text{ \AA}$  respectively, are reported. Corresponding distances in  $[\text{Ag}(\text{Ph}_3\text{P})_3\text{Cl}]$  for one independent molecule are  $2.70$ ,  $2.92$  and  $3.04 \text{ \AA}$  (Table 3). These distances are marked with broken lines in Fig. 2. If a plane is placed through H(6), H(26) and H(42) (Fig. 2), Ag is situated  $2.00 \text{ \AA}$  from the plane and Cl  $0.50 \text{ \AA}$  from it but on the opposite side. If Ag is replaced by Cu the  $\text{Cu}-\text{Cl}$  bond distance should decrease by about  $0.17 \text{ \AA}$  and thereby cause more severe  $\text{H}\cdots\text{Cl}$  interactions. Furthermore, the smaller  $\text{Cu}-\text{P}$  distances should enhance these repulsive interactions. Consequently, if only intramolecular interactions contribute to the differences between the structures the greater  $\text{H}\cdots\text{Cl}$  repulsive interactions in  $[\text{Cu}(\text{Ph}_3\text{P})_3\text{Cl}]$

seem to give rise to smaller  $\text{P}-\text{Cu}-\text{P}$  and greater  $\text{Cl}-\text{Cu}-\text{P}$  angles as compared to the angles in  $[\text{Ag}(\text{Ph}_3\text{P})_3\text{Cl}]$ . However, intermolecular pseudo-graphitic stacking of some of the phenyl rings contributes to the stability of  $[\text{Cu}(\text{Ph}_3\text{P})_3\text{Cl}]$  but the effect of this on the molecular geometry is difficult to account for. In  $[\text{Ag}(\text{Ph}_3\text{P})_3\text{Cl}]$  no pseudo-graphitic stacking of phenyl rings is found. If greater halide ions were introduced into the metal coordination spheres the repulsive  $\text{H}\cdots\text{X}$  interactions should increase for both  $[\text{Ag}(\text{Ph}_3\text{P})_3\text{X}]$  and  $[\text{Cu}(\text{Ph}_3\text{P})_3\text{X}]$ ,  $\text{X} = \text{Cl}, \text{Br}, \text{I}$ . This should probably for the Ag compounds lead to a more regular tetrahedron around Ag, *i.e.* greater  $\text{X}-\text{Ag}-\text{P}$  and smaller  $\text{P}-\text{Ag}-\text{P}$  angles, but for the Cu compounds to a more distorted polyhedron, *i.e.* greater  $\text{X}-\text{Cu}-\text{P}$  and smaller  $\text{P}-\text{Cu}-\text{P}$  angles.

The  $\text{Ag}-\text{P}$  bond distances increase as the number of P atoms around Ag increases.

In  $[\text{Ag}(\text{Ph}_3\text{P})\text{Cl}]$  (Teo & Calabrese, 1976) the  $\text{Ag}-\text{P}$  distances are  $2.376(3)$  and  $2.388(3) \text{ \AA}$ , in  $[\text{Ag}(\text{Ph}_3\text{P})_2\text{Cl}]$  (Cassel, 1979)  $2.467(2)$  and  $2.472(2) \text{ \AA}$  and in  $[\text{Ag}(\text{Ph}_3\text{P})_3\text{Cl}]$   $2.520(1)$ ,  $2.556(1)$  and  $2.552(1) \text{ \AA}$  (Table 2, Fig. 2). This is expected as the accepting ability of Ag decreases with the increasing number of coordinated good-donor atoms.

The  $\text{Ag}-\text{Cl}$  bond distance,  $2.552(1) \text{ \AA}$ , in  $[\text{Ag}(\text{Ph}_3\text{P})_3\text{Cl}]$  is slightly longer than expected ( $2.51 \text{ \AA}$ , Pauling, 1960).

Distances and angles in the coordination sphere of P have expected values. All  $\text{Ag}-\text{P}-\text{C}$  angles are greater than  $109.5^\circ$  and all  $\text{C}-\text{P}-\text{C}$  angles are smaller than  $109.5^\circ$  (Table 2). The mean  $\text{P}-\text{C}$  distance is  $1.825(2) \text{ \AA}$ .

The  $\text{C}-\text{C}-\text{C}$  angles in the phenyl rings deviate little from  $120.0^\circ$  and the mean  $\text{C}-\text{C}$  distances vary between  $1.373(13)$  and  $1.394(3) \text{ \AA}$ .

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## References

- BAUR, W. H. (1972). *Acta Cryst.* **B28**, 1456–1465.  
 BUSING, W. R. & LEVY, H. A. (1957). *Acta Cryst.* **10**, 180–182.  
 CASSEL, A. (1979). *Acta Cryst.* **B35**, 174–177.  
 GILL, J. T., MAYERLE, J. J., WELCKER, P. S., LEWIS, D. F., UCKO, D. A., BARTON, D. J., STOWENS, D. & LIPPARD, S. J. (1976). *Inorg. Chem.* **15**, 1155–1168.  
*International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press.  
 PAULING, L. (1960). *The Nature of the Chemical Bond*, 3rd ed. Ithaca: Cornell Univ. Press.  
 TEO, B. K. & CALABRESE, J. C. (1976). *Inorg. Chem.* **15**, 2467–2473.  
 ZACHARIASEN, W. H. (1967). *Acta Cryst.* **23**, 558–564.